CHAPTER 40

Toxic Hazards of Mining and Smelting

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MINING

Mining is the process of removing mineral resources from the earth. Smelting involves the separation of metallic components of ores and production of metals. Mining is one of the most dangerous occupations. The National Safety Council reported that in the United States in 1995, there were 30 deaths per 100,000 mining workers (a category that includes quarrying as well as oil and gas extraction) as compared with 24 deaths per 100,000 workers for agriculture and 16 for construction workers (1). Most mining deaths are associated with trauma, such as crush injuries, fires, or explosions (2).

The majority of mining injuries are musculoskeletal in origin. For example, in 1994, mining work injuries involving days away from work resulted from trauma in more than 60% of cases (contact with objects and equipment 40.1%, falls 18.9%, transportation accidents 2.9%, slips/trips 1%, fire explosions 0.5%), overexertion in 26.1%, exposure to harmful substances 4.8%, repetitive motion 0.5%, and all others 5.3% of cases. The National Safety Council also reported 1994 annual incidence rates for mining occupational injuries (per 10,000 full-time workers) of 11.8 for disorders associated with repeated trauma, 6.6 for dust diseases of the lungs, 3.0 for skin diseases and disorders, 1.8 for disorders due to physical agents, 1.2 for respiratory conditions due to toxic agents, and 1.4 for all other occupational diseases (1). Mining hazards include exposure to mine gases and dusts, noise, vibration, extremes of temperature and humidity, and less-than-ideal ergometric conditions (3).

In the United States, mining activities are commonly subdivided into the following standard mine classifications:

- Surface metal/nonmetal (metal examples: placer gold mines, porphyry copper mines, iron mines, etc.; nonmetal examples: gypsum mines, asbestos mines, olivine mines)
- Underground metal/nonmetal (metal examples: copper mines, lead/zinc mines, gold mines, etc.; nonmetal examples: marble mines, chromite mines, salt mines)
- Surface coal (strip mining or open pit)
- Underground coal (long wall or conventional)
- Quarries, sand and gravel (e.g., stones quarries, gravel pits)

Most mines are unique in layout and operation, because the geologic environments in which they occur often differ in mineralogy, geologic structure, and physical properties. Therefore, the associated health hazards can differ considerably, even among mines extracting the same mineral.

In principle, the objective of any mine is to extract a geologic resource from the earth in the most economic manner. Surface metal/nonmetal mines are called *open pits* and are designed based on the principle that the value of each block of ore (economically viable part of the resource) extracted from the pit must pay for its mining and processing costs (plus profit margin required), including the cost of removing the waste above it. In coal, surface mines are generally strip mines. Here, if the coal seam is close enough to the surface, then long thin pits are constructed by removing the overburden above the coal, extracting the coal, and then filling the strip pit with overburden from the next pit (Fig. 40-1). In both types of mines, drilling and blasting techniques, extremely large extraction machines (shovels, draglines), as well as transportation equipment (trucks, conveyor belts), are often used. Quarries are often similar in operation to open pit-type mines and use the same types of equipment.

If the resource is too far below the surface to be mined economically as a surface mine, then underground mining methods are the alternative. In underground mining, the layout of the mine is strongly coupled to the geology and structure of the deposit; thus, many underground mines have unique designs. In general, access to the underground is through vertical shafts, inclined ramps, or adits (horizontal tunnel into the side of a hill). In metal and nonmetal mines, development tunnels are driven to the ore body, then large areas called *stopes* are constructed to extract the ore (Fig. 40-2). Many techniques are based on drill, blast, and load mining cycles, whereas others use mechanical

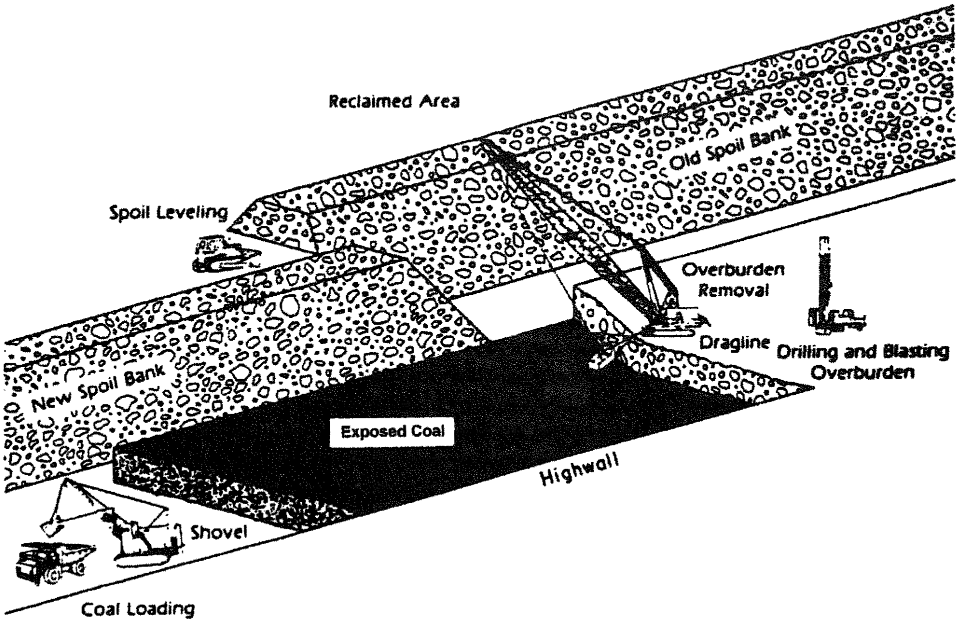

Figure 40-1. Surface mining, opencast method. (Reproduced with permission from Hartman HL. *SME mining engineering handbook,* vol. 1, 2nd ed. Littleton, CO: Society for Mining Metallurgy and Exploration, Inc., 1992.)

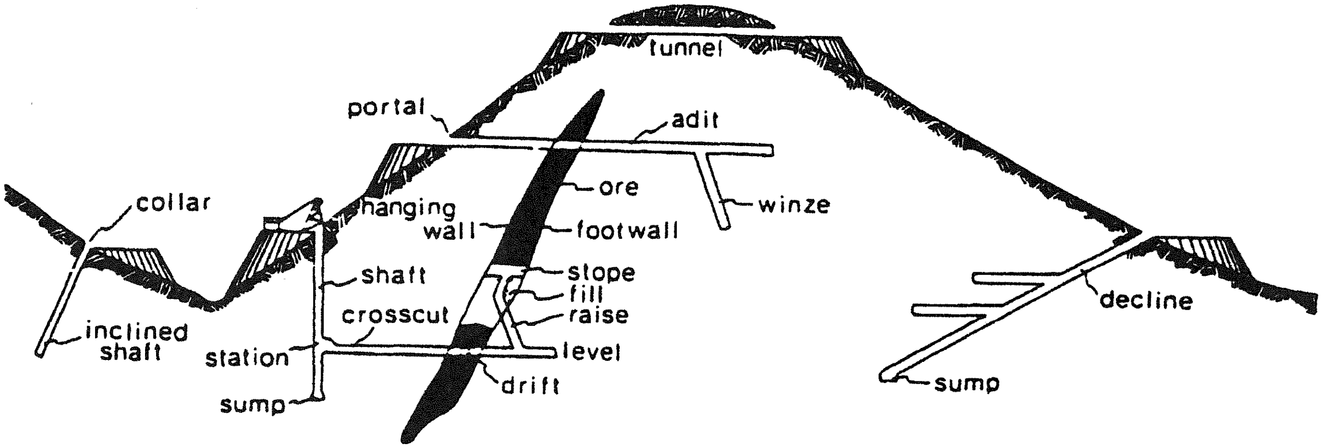

Figure 40-2. Underground mining, stoping method. (Reproduced with permission from Hartman HL. *SME mining engineering handbook,* vol. 1, 2nd ed. Littleton, CO: Society for Mining Metallurgy and Exploration, Inc., 1992.)

excavation machines, such as tunnel-boring machines. In coal, the tabular layout of coal seams and the softness of coal allows miners to use large electrically operated equipment to dig through the coal and transport it using conveyor belts to the surface. These machines can generate a large amount of dust and liberate gases from the coal and host rock. Thus, both underground metal and nonmetal and coal mines use large surface and underground fans to ventilate the workings.

General Mine Hazards

The pick and hammer were the major tools used in early mining methods. However, by the early 1900s, improved open pit and underground mining methods were already under development. New techniques often stressed the introduction of mechanization to improve productivity, which resulted in a decrease in manpower. These increases in mechanization often reduced the number of workers at risk, but also generated new problems such as increased dust levels, vibration, noise, and toxic gases. For example, the introduction of diesel motors produced new gases and particulates into the environment, and individuals were exposed to different explosive fumes through changes in explosive technology.

The mining community has attacked the toxic hazards problem in the mine environment using two approaches. The first is to improve the mine environment directly, and the second provides workers with protective equipment. Improvement in mine ventilation has been the most popular method for improving the underground environment, but continually increasing air velocity has practical limitations. The introduction of regulations—such as controlling the use of diesel engines and the storage and use of explosives—in addition to new techniques to suppress dust and control gases has helped to improve the mining environment.

The enforcement of all regulations for U.S. underground and surface mining operations is conducted by the Mining Safety and Health Administration (MSHA), and similar regulations have been established in other countries. The Federal Mine Safety and Health Amendments Act of 1977 is the basis for these regulations, which can be found in the *Code of Federal Regulations* (*CFR*) section 30. *CFR* 30 regulations allow employees to work for limited periods in concentrations of airborne contaminants that exceed permissible levels if they are protected with appropriate respiratory protective equipment. Respirators approved by National Institute for Occupational Safety and Health under *CFR* 42, part 84 are regulated. Thus, the use of materials such as respirators and protective clothing has also improved individual protection for workers. In general, surface mines have much lower overall exposures to toxic substances than experienced in underground mines, except possibly for exposure to dusts.

Mine Dusts

Dust hazards were severe in mining history and contributed to extensive deaths from dust-related diseases. Several important factors influence the probability of a miner's developing a dust-related illness, including the nature of the dust (e.g., mineralogy, particle size, toxicity), quantity of dust, length of exposure, period since first exposure, and individual susceptibility. In modern mines, dusts are still important because of safety issues related to reduced visibility, dust-induced chronic lung diseases, irritation effects, and other toxic effects.

Pneumoconioses are a set of lung diseases that include silicosis, asbestosis, coal-workers' pneumoconiosis, and other fibrotic lung diseases resulting from inhalation of dusts. This section contains an overview of mineral types, geologic factors, mine environments, and health issues related to the extensive topic of pneumoconiosis-producing dusts.

SILICA AND SILICOSIS

Exposure to dusts containing free silica (SiO_2) are associated with pulmonary injury. Free silica mineral species encountered in mining operations are quartz and tridymite, which are crystalline; cristobalite and chalcedony, which are microcrystalline; and diatomite and opal, which are amorphous. Exposure to silica dusts is possible whenever free silica is encountered in mining operations, and in particular during mining activities that include drilling, blasting, transportation, maintenance work, assaying, crushing, and milling.

Quartz is the most common mineral in the earth's crust and is often the major component of rocks encountered in mining and quarrying of the following materials:

- Base and precious metal ores in quartz-carbonate veins and some sedimentary and volcanic rocks
- Quartzite and sandstone
- Uranium ore in conglomerate and sandstone
- Placer deposits
- Mica
- Feldspar and mineral deposits in pegmatitic and granite rocks

- Coal
- Banded ironstone
- Sands and gravels
- Granites

It should be noted that even though free silica may not occur in the ore being mined, it often is present in the host rock and is therefore an important component of the mining operation. Cristobalite is common in siliceous igneous rocks. Chalcedony is finely crystalline silica and is found in coal deposits as nodules, in banded iron formations, and sometimes in shales and limestones. Amorphous silica is often found in opal deposits and in flints and cherts.

Prolonged inhalation of particulate matter containing free silica can result in silicosis. The clinical features of silicosis have been studied and documented by many authors (4–6) and will not be discussed here. Mining experience has shown that even though an individual can contract silicosis on the first dust exposure, the average time before detection is after 20 years of exposure (7,8). Silica dust remaining in the lungs may also cause silicosis many years after removal from the mining environment (9). Silica exposure has been associated with the development of chronic obstructive pulmonary disease, although this is a controversial finding (10). Exposure to crystalline silica may increase the incidence of lung cancer (11).

ASBESTOS AND ASBESTOS-RELATED DISEASES

Asbestos minerals are fibrous in nature and are subdivided into serpentine and amphibole classifications. The six main varieties of asbestos are chrysotile, which is serpentine, and tremolite, anthophyllite, actinolite, amosite, and crocidolite, which are amphibole. Chrysotile, amosite, crocidolite, and anthophyllite are the four that are of commercial value, and 95% of world production comes from chrysotile. The majority of asbestos is mined underground, where adequate ventilation and use of personal protective equipment are important in limiting exposure. It should be noted that during mining, the asbestos fibers are often bound together geologically, which limits the generation of the short fibers associated with asbestos-related diseases. However, the milling process breaks up the fibers and results in a considerably more dangerous environment.

Health effects from asbestos exposure have been well documented, and numerous review articles provide a detailed description of asbestos-related diseases (12–15). Asbestosis is the main threat to miners who have a prolonged exposure to elevated dust concentrations of all varieties of asbestos dust. Asbestos exposure increases the risk of primary lung cancer among miners (15). Primary malignant mesothelioma has been reported among crocidolite miners (16) but has been seen rarely when mining other asbestos varieties.

COAL AND COAL-RELATED PNEUMOCONIOSIS

Coal is generally ranked geologically according to criteria such as carbon content. The highest rank is anthracite, followed in decreasing order by bituminous coal, subbituminous coal, and lignite. The hardest coals have the highest ranks, contain the lowest amount of volatile matter, and generate the greatest amount of heat when burned. The coal rank and seam thickness often influence the type of dust exposure for the miner. Miners working in thin seams often have more contact during the mining process with rock strata adjacent to the coal seam. Many coal deposits can contain free silica in the shale and sandstone beds that neighbor the seam. Thus, the degree of hazard cannot be ascertained solely by knowledge of quartz with the coal itself.

Inhalation of coal mine dust can lead to coal workers' pneumoconiosis and silicosis, in addition to increased rates of industrial bronchitis and emphysema. Simple coal workers' pneumoconiosis and progressive massive fibrosis may occur. Considerable literature and data exist relating to these coal-related diseases (17–19). The place of work and type of operation affect the extent of exposure for the miner. Cutting machine operators and their helpers at the coal face experience the highest dust concentrations. Miners performing maintenance work, such as electricians and mechanics, as well as surface workers, are generally exposed to less dust.

NUISANCE DUSTS

Nuisance dusts are mineral or other dusts not shown to have adverse health effects. However, gross overexposure can overload protective respiratory mechanisms, and nuisance dusts should not be considered entirely harmless at any concentration. Dust particles in the respirable size range are more likely to result in adverse health effects. Examples of nuisance dusts found in mining include Portland cement, gypsum, kaolin, limestone, calcium carbonate, fibrous glass, and marble. These dusts are considered to be nuisance dusts if they do not contain any toxic impurities—for example, less than 1% quartz. Studies of exposure to dusts generated from mining or quarrying calcium carbonate rocks indicate little or no disease of the lungs (20). Free silica or silicates, which may be found with limestones and dolomites, can harm the lungs.

Radiation Exposures

Excess lung cancer has been well described in uranium miners (21). However, uranium mines are not the only mining environments in which radioactive contaminants are found. Measurements in gold, copper, lead and zinc, coal, limestone, phosphate, and more than 20 other types of mines have indicated significant radon daughter concentrations (22,23).

The radioactive decay chains of uranium and thorium are of concern in mining. Uranium is common in the earth's crust, and its decay chain includes radium (^{226}Ra), which is the parent of radon (^{222}Rn). The thorium decay chain contains an isotope of radon (^{220}Rn) called *thoron*, which can be a problem in any mine in which thorium minerals exist. Thoron behaves in the same manner as radon, and thorium daughters present the same cancer risk as radon daughters. A complete description of radon and radon daughter buildup and decay is available elsewhere (24).

In the underground mine atmosphere, radon and thoron concentrations vary considerably in space and time. In the steady-state geologic form, diffusion of thoron and radon is low. However, mining activities, such as blasting and material handling, can strongly influence concentrations (25). Even after mining is terminated, changes in barometric pressure can generate high radon concentrations. The control of airborne radiation can be attained by preventing or retarding their flow into the mine ventilation system by confinement techniques such as seals or bulkheads. Alternatively, ventilation can be used for diluting and removing the contaminated air.

Radiation monitoring is essential in mines to ensure an effective radiation control program. U.S. regulations (*CFR* 30, 57.5038) provide for an annual exposure limit of 4 working level months (WLM) for radon daughters (one working level month equals 170 hours of exposure to one working level). This relates to an average radon daughter concentration of 0.33 working level (WL), which equals 1.3×10^5 mev potential alpha energy from radon daughters per liter of air. In radon daughter environments exceeding 1.0 WL, respirators must be worn as a temporary measure (*CFR* 30, 57.5044), and respirators that remove radon and its daughters or provide fresh air must be worn in radon daughter

TABLE 40-1. Common mine gases

Gas	TLV-TWA[a]	Density[b]	Odor	Toxicity	Comments
Carbon dioxide	5,000 ppm	1.53	None	Asphyxiant	Toxic at higher concentrations
Carbon monoxide (whitedamp)	25 ppm	0.97	None	Chemical asphyxiant	Primarily from incomplete combustion
Hydrogen sulfide (stinkdamp)	10 ppm	1.19	Rotten eggs[c]	Irritant, chemical asphyxiant	Flammable range, 4–44%
Hydrogen	—	0.07	None	Flammable	Flammable range, 4–74%
Methane (firedamp)	—	0.55	None	Simple asphyxiant	Flammable range, 5–15%
Oxides of nitrogen	NO 25 ppm; NO_2 3 ppm	1.04; 1.58	Difficult to detect	Respiratory irritant	Poor warning properties, delayed pulmonary injury may occur
Radon	—	—	None	Carcinogenic	Not limited to uranium mines
Sulfur dioxide	2 ppm	2.26	Metallic	Irritant	Good warning properties

[a] American Conference of Governmental Industrial Hygienists Threshold Limit Value–Time Weighted Average.[31]

[b] Density of air = 1.

[c] Causes olfactory fatigue at concentrations exceeding 50 ppm.

concentrations higher than 10 WL (*CFR* 30, 57.5046). At least one radon daughter sample must be acquired in the exhaust airway of all U.S. mines and additional samples collected if a concentration greater than 0.1 WL is collected. Studies of MSHA data for 1985 through 1987 demonstrated 139 mines in the United States at a working level of 0.1 WL or more for radon daughter concentrations (23). Exposure of mine and mill workers to beta and gamma radiation has not been considered important for 0.1% to 1.0% grade U_3O_8 ores (26). However, there has been some concern of exceeding the 5 rem annual exposure level for external whole-body radiation when working with 1% to 5% U_3O_8 ores (27).

Mine Gases

The hazardous gases encountered in mines vary depending on the characteristics of the individual mine. Determinants include the mineral content of the ore, gases naturally present in the strata being mined, presence of organic debris, and mining equipment and procedures. Oxygen deficiency and excesses of carbon dioxide, carbon monoxide, methane, oxides of nitrogen, sulfur dioxide, hydrogen sulfide, diesel exhaust, and hydrogen are potential causes of miner morbidity and mortality. Common mine gases are listed in Table 40-1.

Oxygen deficiency, also known as *blackdamp*, can occur in poorly ventilated underground mines with decomposing organic material or reducing ores (3). Oxygen deficiency is defined by the Occupational Safety and Health Administration as less than 19.5% by volume (28). In individuals without significant underlying illness, respiratory symptoms occur at concentrations of less than 16% and unconsciousness at concentrations of less than 10% (29). Symptoms vary at a given oxygen concentration depending on the extent of worker exertion.

Carbon dioxide is a colorless gas with a slightly acid taste at high concentrations. Sources include mine personnel, flame safety lamps, fires, diesel engines, blasting operations, and occasionally coal and adjacent strata. Adverse health effects increase with higher concentrations. According to the U.S. Department of Labor's Mine Safety and Health Administration, 0.5% (5,000 ppm) increases ventilation, 3% doubles ventilation, and 10% is only tolerated for a few minutes at rest (29).

Carbon monoxide is a colorless, tasteless gas. Sources include diesel engines, fires, explosives, and offgassing from certain coals. Carbon monoxide acts as a chemical asphyxiant, interfering with oxygen transport by hemoglobin and through inhibition of the cytochrome oxidase system. Five hundred ppm (0.05%) can be fatal in 3 hours (29). The rate of interaction with blood increases with exertion.

Methane is the most common flammable gas found in mines and is produced primarily by coal and adjacent strata. Accumulation of methane has resulted in numerous explosions in underground and surface mines, and there have been more than 10,000 deaths in the last 60 years from methane-related explosions (29). Methane also acts as a simple asphyxiant by displacing oxygen from the air. Other hydrocarbons found in mines include ethane, propane, and acetylene, usually present in trace amounts. These also are potentially flammable and act as simple asphyxiants.

Oxides of nitrogen include nitrogen dioxide (NO_2), nitric oxide (NO), and nitrogen tetroxide (N_2O_4). They are formed at high temperatures by diesel and gasoline engines, fires, explosives, electrical discharge, and blasting. Because of their relatively low water solubility, they have poor warning properties. On inhalation they can reach the lower respiratory tract, causing delayed pulmonary damage.

Sulfur dioxide is a colorless irritating gas with a pungent sulfurous smell. Sources include fires that involve iron pyrites and blasting for certain sulfide ores. Sulfur dioxide is very water soluble and has good warning properties. It causes primarily upper respiratory tract and mucous membrane irritation, but at higher concentrations can also cause lower respiratory tract injury.

Hydrogen sulfide is a colorless, flammable, irritating gas, is heavier than air, and has an odor of rotten eggs at low concentrations. It is formed through blasting for sulfide ores and also occurs naturally in gas, oil, and coal fields. Hydrogen sulfide can act as an irritant as well as a chemical asphyxiant. Prolonged exposure increases the odor threshold through olfactory fatigue, which generally occurs above 50 ppm.

Diesel exhaust contains aldehydes, oxides of nitrogen, carbon monoxide, and particulates. Diesel exhaust is quite irritating and has been associated in some studies with an increased risk of lung cancer (30). Underground, scrubbers are used on diesel equipment to clean the exhaust. Hydrogen is colorless and tasteless and is not normally present in significant concentrations in mine air, except in the vicinity of battery-charging stations or after fires and explosions. Radon and radiation hazards are further described in the section Radiation Exposures.

General Safety Devices and Protective Equipment

The most appropriate solution for limiting exposure to toxic hazards is to use engineering control techniques. However, the dynamic nature of mines means that the layout is continually changing and the environmental engineering control techniques may not always work as planned. Monitoring programs are needed to determine the state of the environment, and personal protective equipment must often be used to protect miners, especially during times of transition.

Many mines use sophisticated sampling and measurement devices to determine gas and dust concentrations in the mine environment. To determine concentrations of harmful noxious or poisonous gases, *CFR* 30 requires detectors or laboratory analysis of mine air samples. Threshold limit values as specified by the American Conference of Government Industrial Hygienists are used to define acceptable limits (31). Handheld methane detectors, portable oxygen monitors, and flame safety lamps are used on a daily basis by miners. In underground coal mines, *CFR* 30 requires that regular testing for oxygen deficiency be made with an MSHA-approved and appropriately maintained permissible detector capable of detecting 19.5% oxygen with an accuracy of ± 0.5%. Handheld devices are commonly used for measuring concentrations of explosive gases, such as carbon monoxide (limit 2.5%), methane (limit 1.0%), hydrogen (limit 0.8%), hydrogen sulfide (limit 0.8%), acetylene (limit 0.4%), and propane (limit 0.4%). Detector tubes for measuring concentrations of toxic and noxious gases can be used in mines but are often only accurate within 25% of the actual reading. MSHA-approved portable self-contained detection instruments for gases such as nitric oxide and nitrogen dioxide can also be used. To determine dust exposures, a large array of MSHA-approved personal dust samplers are commonly used in U.S. mines.

Environmental monitoring systems are commonly found in underground coal mines and less frequently in underground metal and nonmetal mines, and have been used to continuously measure environmental parameters such as carbon monoxide, carbon dioxide, methane, hydrogen, oxides of nitrogen, hydrogen sulfide, and oxygen. If concentration limits for any of these parameters are approached or exceeded, then the monitoring system registers an alarm to alert the miners. In addition, if ventilation parameters such as airway pressures, airway velocities, and fan operations are also measured by the monitoring system, then the system can react to changes in the mine to maintain a healthy underground environment. It should be noted that atmospheric monitoring systems are not commonly found in surface mines, except possibly in enclosed surface structures, such as conveyor belt runs, mineral processing facilities, and workshops.

When engineering control techniques are not capable of maintaining a healthy mine environment, personal-protection devices can be used. For dust exposure, filter-type face masks are frequently used in the mining industry (32). Popular varieties of powered respirators include face masks, helmets, helmet air curtains, and canopy air curtains. The powered respirators are more often used at the mining face, where excessive dust generation can often be a problem. Abnormal gas conditions in underground mines can occur from outbursts of strata gases (carbon dioxide, methane, nitrogen), interruption of mine ventilation, fires, explosions, and excessive mining rates. In the event of an abnormal gas event, then respiratory protection using devices such as the gas mask, carbon monoxide self-rescuer, and self-contained self-rescuer must be provided. These are mostly temporary devices that allow the miner to escape from the affected working area. Self-contained breathing apparatuses are used primarily for rescue operations.

Mining Wastes

In 1990, mining and ore beneficiation processes generated an estimated 2 billion metric tons of solid waste in the United States, nearly one-half of which was unprocessed overburden removed to access ore. *Beneficiation* is crushing and grinding of ore to facilitate concentration of the raw material of interest by flotation. The waste product is slurried to impoundments that are an average of 500 acres in size. *Tailings* are the solid particulate result of evaporation at these sites. Only a small number of Comprehensive Environmental Response, Compensation, and Liability Act Superfund listings are minerals industry waste sites, said to be mostly a result of past rather than current industry practices (33).

TABLE 40-2. Mineralogical composition of copper cliff tailings

Feldspar	+50.0	M A1(Al,Si) O8, M = K, Na, Ca, Ba, NH4
Chlorite	20	M6(Al,Si)O10(OH)8, M = Mg, Fe2+, Fe3+, Mn
Quartz	10	SiO2
Pyroxenes	7	ABSi2O6, A = Na, Ca, Mg, Fe2+, B = Mg, Fe2+, Al
Biotite	7	K(Mg,Fe)3(Al,Fe)Si3O10(OH,F)2 (a mica)
Pyrrhotite	5.6	Fe1-xS
Magnetite	0.6	Fe3O4
Pentlandite	0.5	(Fe,Ni)9S8
Chalcopyrite	0.3	CuFeS2

Note: Zinc is also recovered from the ore, and although it isn't listed in the analysis, it is a significant soil contaminant around the plant.

The main focus of popular attention to mining wastes has been unsightly mounds of tailings and resulting airborne dust, although there is considerable potential for direct human toxicity by contamination of both ground- and surface water, which may be absorbed by crops or ingested by domestic animals or humans. Concentration of heavy metals in mine and tailings runoff water is enhanced by acidity in rain and inherent acidity of ores and tailings (34). Copper tailings may contain from a few ppm to several thousand ppm of arsenic, cadmium, chromium, copper, lead, zinc, beryllium, and silica. Gold, lead, and molybdenum tailings may additionally include other trace elements, such as silver, selenium, mercury, molybdenum, manganese, and iron (35). Airborne wastes, if uncontrolled, may also cause community toxicity. High indoor air radon concentrations have been documented in homes built on uranium tailings (36). In one of the most notorious examples of environmental exposure from mining wastes, an increase in cadmium concentration in rice was documented in the Jinsu River basin in Japan, downstream from a cadmium-zinc-lead mine. Ingestion of the rice was associated with epidemic Itai-Itai disease, consisting of severe bony deformities and chronic renal disease in villages with the highest rice-cadmium concentrations (37). An example of mineralogic composition of copper tailings is listed in Table 40-2.

SMELTING

The production of metals involves mining, concentration, and reduction to a metallic form. *Smelting* is defined as the melting or fusing of ores to separate the metallic components. Additional steps in the reduction of metals include roasting, calcining, sintering, converting, and refining, which are considered part of the overall smelting process.

There are two major smelting techniques: pyrometallurgy and hydrometallurgy. These techniques may be combined in smelter operations. A common preparatory step for pyro- and hydrometallurgy is concentrating the ore by crushing and using separation techniques. Pyrometallurgy involves heating of the ore to temperatures sufficient to reduce metal oxides to their

TABLE 40-3. Potential toxic exposures in smelters

- Aluminum smelters
  - Carbon monoxide
  - Cryolite (Na_3AlF_6) dust
  - Fluoride (gaseous and particulate)
  - Polycyclic aromatic hydrocarbons
  - Sulfur dioxide
- Copper smelters
  - Arsenic
  - Cadmium
  - Lead
  - Sulfur dioxide
- Lead smelters
  - Arsenic
  - Cadmium
  - Chlorine gas
  - Copper
  - Lead
  - Sulfur dioxide
  - Zinc
- Nickel smelters
  - Ammonia (hydrometallurgic process)
  - Carbon monoxide
  - Hydrogen sulfide
  - Nickel
  - Nickel carbonyl
  - Sulfur dioxide
- Zinc smelters
  - Antimony
  - Arsenic
  - Cadmium
  - Carbon monoxide
  - Copper
  - Lead
  - Manganese
  - Zinc

metallic form. There are a variable number of steps in this process, depending on the specific ore and smelter. In hydrometallurgy, metal ores are processed through chemical treatments. The initial step is usually leaching, which may require the addition of electricity or heating. The ore may also be roasted before leaching. The leaching solution is then treated by electrolysis or further chemical treatment to reduce and remove the metals from solution.

The potential toxic exposures from smelters are numerous and vary among smelters. A partial list of potentially hazardous exposures is found in Table 40-3. The initial concentrating step and loading/unloading and transfer of the metal ores lead to particulate generation and the potential for worker exposure. Roasting, melting, and converting the metal ore can produce a variety of hazardous exposures, including sulfur dioxide and contaminants present in the ore (such as arsenic). The high temperatures and high noise level in the smelters also contribute to safety hazards. This chapter focuses on smelting of aluminum, copper, lead, nickel, and zinc.

Aluminum

Aluminum is produced primarily from bauxites, which contain a variable amount of alumina, kaolinite, and clay minerals. The bauxite is crushed, washed, and dried before refining. The bauxite is then heated and pressurized with caustic soda to form sodium aluminate, which is separated out and recovered.

Aluminum smelting involves reduction of alumina by an electrolytic process. The cathode is composed of coal and coal tar pitch. The anode is composed of coke and coal tar pitch and is used up as the electrolytic process continues. There are two major processes: Soderberg and prebake. The Soderberg process involves addition of coke and coal tar pitch to the anode in the smelter. It generally results in more worker exposure, with the horizontal-stud Soderberg cells emitting approximately six times more polycyclic aromatic hydrocarbons (PAHs) than vertical-stud cells (3). Prebakes are large carbon blocks that are manufactured outside the smelter and heated to remove the pitch and other contaminants in controlled conditions before transport. New smelters are almost entirely using the prebaked anodes, which produce less pollution and are more energy efficient.

In the smelter, alumina is dissolved in molten cryolite (Na_3AlF_6) baths called *pots*. Fluorspar (CaF_2) and aluminum fluoride (AlF_2) are added to reduce the melting temperature and to increase process efficiency (3). Alumina is added to the pots by opening a mechanically operated door after the surface crust is broken so the additional material can mix. A direct current is driven through the bath, maintaining a 960° to 980°C temperature, and the alumina is reduced to molten aluminum, which falls to the bottom of the bath. The aluminum metal is tapped every 24 to 48 hours by sucking it into a crucible. This process produces 99.8% pure aluminum.

Potential toxic hazards in the aluminum smelting industry include fluoride exposure from both gaseous and particulate sources, including cryolite dust, carbon monoxide, sulfur dioxide, and coal tar pitch volatiles (CTPVs), which include PAHs, heat stress, and electromagnetic radiation from the high direct current (DC) fields (3). The CTPVs and PAHs are produced from the consumption of the carbon and pitch anode. Sulfur dioxide, carbon monoxide, and carbon dioxide may also be produced from consumption of the anode. Typically, tapping, crust breaking, and anode changing are associated with increased exposure to emissions from the pots. Anode tenders have relatively greater exposures to sulfur dioxide and hydrogen fluoride than other smelter workers. Crane operators have the potential for significant toxic exposures and therefore often work in a contained cab with a separate ventilation system. Electrocution can occur if a worker touches the cathode leads and either another row of pots or the outside wall. Explosions can occur if a liquid container (e.g., a soda can or larger) is dropped into the pot, generates superheated steam, and explodes. Exposure to chlorine gas may occur in the casting plants, in which it is used to clean out casting furnaces (38). Noise exposure is the greatest in rod mills, although crust breakers may be as noisy as 95 dB.

Respiratory and carcinogenic effects have been described in aluminum smelter workers. Accelerated loss in lung function has been noted, although this problem may be prevented by improvements in working conditions (39). Although very controversial, both *de novo* asthma and exacerbation of underlying asthma have been reported. Hydrogen fluoride and other fluoride-containing chemicals have been implicated, along with respirable dust, sulfur dioxide, and CTPVs (38), and symptoms are seen in association with working close to fumes and dust when pot hoods are removed or during removal of hot anode blocks (40). Chronic obstructive pulmonary disease has also been associated with long-term exposure in aluminum smelters (38). The incidence of Shaver's disease, characterized by pulmonary fibrosis and emphysema, has been practically eliminated by improvements in workplace conditions through decreases in abrasive alumina and silica particulates. Elevated rates of bladder cancer and lung cancer have been reported (41).

Copper

Copper oxide or sulfide ore is usually ground in a ball mill to form a slurry, and additives are used to assist in the flotation of the copper-containing component. The separated component is then dried and transported for smelting as a 16% to 32% concentrate (3). Hydrometallurgic and pyrometallurgic smelting techniques are used. At most smelters, ore concentrate is roasted with air at approximately 1,000°F to remove impurities such as sulfur—and to a lesser degree, arsenic—by conversion to oxides. The resulting product is called *calcine*. Roaster emissions are run through electrostatic precipitators to separate out dust and aggregated fumes. The calcine is then heated with silica flux to high temperatures (greater than 2,000°F), usually in a reverberatory or electrical furnace, to convert copper oxide to copper sulfide and to further remove impurities. Other furnaces used include flash furnaces and Noranda reactors. In the furnaces, iron oxide is produced and rises up as slag, which is separated off. The copper matte is tapped and transported in large ladles to be poured into converters. In the converters, a silica flux is added, and air is blown through the mixture to convert the remaining iron sulfide to iron oxide (which is removed as slag) and to convert the copper sulfide to copper. Converter sulfur dioxide emissions are often collected for production of sulfuric acid, and copper-containing offgases are recovered and recycled. The more highly purified blister copper—named for the small bubbles of sulfur dioxide remaining in the copper—is then transferred to an anode furnace for additional refinement using air and natural gas. Electrolysis in a copper sulfate–sulfuric acid bath may be used to further purify the metal.

Potential exposures at copper smelters include arsenic, sulfur dioxide, lead, silica, heat, and noise, and to a lesser extent aromatic hydrocarbons, carbon monoxide, antimony, and cadmium. Most arsenic is transformed into arsenic trioxide during smelting. Copper smelter workers have been shown to have high urine arsenic concentrations (42). The greatest concentration of arsenic is found in flue dust, and thus those individuals collecting the dust and cleaning the flues are at high risk of exposure. Sulfur dioxide is produced during the oxidation of the copper ore, which contains an appreciable amount of sulfates. Inorganic sulfate-metal ion complexes have also been measured and may have different toxicologic properties than sulfur dioxide alone (43). Carbon monoxide is also formed from combustion. Dusts and fumes may contain silica, lead, cadmium, and molybdenum. Aromatic hydrocarbons may be produced during the use of electric furnaces and anode refining (44). Crane operators are at significant risk for exposure unless adequate respiratory protection is provided. Maintenance of ventilation and pollution control equipment can result in significant exposures to most of the hazardous materials previously described, often in a concentrated form. Areas requiring maintenance include flues, cyclones, wet-collectors, baghouses, electrostatic precipitators, and the acid plants. Maintenance is also required for general smelter operations and may potentially result in high exposures to contaminants.

Injuries reported in copper smelters have historically included acid skin burns, septum perforations from arsenic exposure, and inhalation injury from sulfur dioxide. An increase in lung cancer has been well documented (45–49), and work at the roasters and gas purifiers appears to carry a higher risk for developing lung cancer (50,51). Elevated lung cancer rates are felt to be related to cumulative arsenic exposure and not to sulfur dioxide exposure (52,53). Smelter arsenic exposure has also been correlated with respiratory cancer mortality (54), as well as increases in large intestine and bone cancer (55). Excesses in cardiovascular disease have also been reported (56). Raynaud's phenomenon and vasospastic reactivity have been described in association with smelter arsenic exposure (57).

Lead

Lead-bearing ore, primarily galena, is crushed and ground to a uniform size. Additives such as sodium carbonate, lime, copper sulfate, pine oil, cresylic acid, xanthate, and sodium cyanide may be used to prepare the lead concentrate (3). The concentrate is sintered to convert sulfur to sulfur dioxide and lead sulfide to lead oxide. The sinter is combined with coke and fed into a blast furnace, in which the lead is melted and reduced to its metallic form. The lead bullion is cooled, and most of the copper separates out. Any remaining copper is removed from the lead by the addition of sulfur before refining. Refining can be pyrometallurgic or hydrometallurgic, with the former predominating. The lead bullion is heated and oxidized to remove arsenic, antimony, and tin. Zinc is added to remove gold and silver, and then the zinc is removed by distilling at 600°C. The lead undergoes additional processing to remove impurities. Hydrometallurgic refining involves the use of fluorosilicates or molten sodium hydroxide and sodium nitrate (3).

The major toxic exposure in lead processing is lead dust. Additional potential hazards include exposure to arsenic, sulfur dioxide, cadmium, copper, indium, and zinc. Chlorine gas added to dezinc the lead may also pose an exposure hazard. Lead smelter workers have been reported to have increased renal disease, cerebrovascular disease, and adverse effects on spermatogenesis (58,59). Smelter lead exposure may result in a very slight increase of risk for some malignant neoplasms (60,61).

Nickel

Nickel-containing ores include sulfides, oxides, and silicates. The sulfide ores are concentrated through crushing, grinding, and flotation. Further processing varies but generally involves flotation, roasting, addition of flux and smelting, and either electrolysis or further chemical or pressure/heat treatment, depending on the associated metals found in the zinc-bearing ore. Roasting oxidizes iron sulfides to iron oxide and produces sulfur dioxide. Smelting typically occurs in reverberatory furnaces, and the matte is further processed in converters. The resulting mixture contains a number of different metals and is allowed to cool and crystallize. This is crushed and ground, and the nickel and copper sulfide components are removed and separated by flotation. The nickel sulfide is oxidized and may be treated with chlorination followed by hydrogen to remove copper and then reduce the nickel. Further purification can be achieved through electrolysis or combination with carbon monoxide to form nickel carbonyl, which is decomposed at higher temperatures to produce metallic nickel. Alternatively, hydrometallurgic processes may be used. Nickel oxide and nickel silicate ores are reduced using gypsum or sulfur-containing petroleum products during roasting and smelting and are further refined in converters. Hydrometallurgic procedures may also be used for these ores, involving the use of ammonia to leach the nickel, followed by further processing.

Potentially hazardous exposures can occur from the sulfur dioxide produced by the oxidation of sulfur or sulfates. In certain metallurgic processes, carbon monoxide and nickel carbonyl are used. Both are colorless and have poor warning properties, making these chemicals extremely hazardous. In hydrometallurgic smelting, ammonia is added under pressure to furnace matte to leach soluble metals, and hydrogen sulfide may be added to precipitate sulfide slurries. Exposure to nickel in smelters can result in allergic reactions, including dermatitis and rhinitis (62). Nickel refinery workers previously had a greatly elevated risk of mortality from lung cancer and carcinomas of the nasal sinus, but with improvements in working conditions, this increased mortality had resolved in at least one study (63).

Zinc

Zinc-bearing ore is usually in the sulfide form. It is concentrated through the use of crushing and grinding, followed by flotation using a small amount of pine oil and air agitation to float the mineral sulfides so they can be skimmed off. Additional flotation steps may be used to further concentrate the zinc. The zinc sulfide is converted to zinc oxide and sulfur dioxide through roasting, commonly in a fluidized-bed roaster. Sintering may follow in certain operations to remove contaminants and produce particles of a desired size. Contaminants produced in sintering may include cadmium and lead. Alternative processes are used for zinc oxide ores and secondary zinc-bearing metals, often using coal to reduce the zinc to a metallic form. Further processing involves the reduction of the zinc oxide through the combustion of coke and natural gas at temperatures of at least 1,000°C, producing volatilized metallic zinc and carbon monoxide. Hydrometallurgic processes are being used more frequently and involve leaching the zinc concentrate with sulfuric acid and further purification before electrolysis.

Exposure to zinc fume can result in metal fume fever. Lead, arsenic, and cadmium are common contaminants in zinc-bearing ores, and overexposure to these metals may occur. Often zinc and lead smelting are run in parallel. Most cadmium is produced from smelting and refining zinc ores, and zinc ore concentrates commonly contain 0.2% to 0.3% cadmium. Cadmium has been classified by International Agency for Research on Cancer as a confirmed human carcinogen (64). Copper, antimony, indium, germanium, and gallium may also be present and may be released during the smelting process. Lead, cadmium, and indium specifically may be volatilized during sintering. Zinc ores are also commonly found in the sulfide form, and sulfur dioxide is produced by oxidation during roasting. Carbon monoxide can be formed during zinc reduction.

Environmental Contamination

The effects of smelter emissions on nearby populations are well documented. Sulfur dioxide is a common waste gas from the smelting process. Many metals are present in complex with sulfates, and the oxidation during heating with oxygen produces sulfur dioxide. Other sulfur species are also produced during smelting and may be important respiratory irritants. The sulfur may complex with metal-containing aerosols, forming stable transition metal complexes, with the rate of formation dependent on the acidity of the mixture. Iron and copper complexed with sulfur dioxide have been measured in smelter plumes from copper and lead smelters (43), and these complexes may be more toxic than sulfur dioxide alone (65).

Soil and produce concentrations of cadmium, copper, and lead were found to increase with proximity to a smelter in Manitoba (66). Urinary arsenic levels were higher in residents living near a copper smelter than those living farther away, and this relationship was more marked in residents younger than 7 years old (67). Children aged 0 to 6 living within one-half mile of a copper smelter in Washington State had elevated urinary arsenic levels (68). In Port Pirie, Australia, blood lead concentrations of children were related to both soil lead concentration from a nearby smelter and father's employment at the smelter (69). Blood lead levels higher than 40 μg per dL were found in 53% of children aged 1 to 9 years living within 1.6 km of a lead smelter in El Paso, Texas (70). Blood lead levels in pregnant women were related to living distance from a large lead smelter (71). However, there was no relation of maternal blood lead with infant birthweight, length of gestation, or preterm delivery (72). Effects on animals are also found. The soil concentrations of copper, lead, and zinc were found to increase with proximity to a zinc smelter in Peru, and increased hepatic concentrations of arsenic, cadmium, lead, and manganese were found in sheep grazing near the smelter (73).

Reducing Toxic Exposures

Reducing worker exposure can be considered most easily during the design of a new smelter. Handling of crushed materials can be automated and contained to prevent spread of dusts. The use of hazardous materials can also be automated to minimize human exposure. Easy access for maintenance can be planned. Less toxic processes, such as using hydrometallurgy rather than pyrometallurgy, can decrease overall exposures. For established smelters, continued safety training and use of protective devices such as respirators can improve worker safety. Industrial hygiene surveys can identify exposure sources and suggest methods of minimizing exposures. Medical monitoring of employees can alert management to any occult problems and prevent the development of debilitating chronic diseases. This may include monitoring for heavy metals and periodic pulmonary function tests. Monitoring devices located near hazardous materials sources can be set to alarm if concentrations exceed set standards. More effective pollution control devices can decrease nearby population exposures. Additional improvements will most likely result from continued changes in smelter design and equipment, as well as from continued strengthening of occupational and environmental standards in association with adequate enforcement.

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CHAPTER 41

Pneumoconioses

Feroza M. Daroowalla

The term *pneumoconiosis* is defined by the International Labour Office (ILO) as the accumulation of dust in the lungs and the tissue reactions to its presence. It refers to nonmalignant fibrosis and scarring of the lungs in reaction to environmental or occupational exposure to inorganic dusts, such as silica, asbestos, tin, and coal dusts (1). Dusts that result in fibrogenic pneumoconiosis are as follows:

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